PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application of:

Applicants : David B. Smathers, Francis S. Valent, and Michael J. Regan
Serial No. : 10/527,513
Filed : October 26, 2005
Title : PROCESS FOR MAKING DENSE MIXED METAL Si_3N_4 TARGETS
Docket : 020324 223P2
Examiner : Jie Yang
Art Unit : 1793
Customer No.: 33,805

Mail Stop Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Sir/Madam:

Declaration Under 37 CFR §1.56

I, David B. Smathers, do declare that:

[0001] I am one of the named co-inventors of the above application and am employed by one of the joint owners of the application, Tosoh SMD, Inc. (TSMD). The other inventors of the application are Francis S. Valent, employed by TSMD, and Michael J. Regan, employed by the Hewlett-Packard Company (HP).

[0002] The present application is a United States national filing of PCT International Application WO 2004/024452 filed August 27, 2003. The PCT International Application claims the benefit of U.S. Provisional Patent Application 60/410,607 filed September 13, 2002 (priority date).

[0003] Upon review of the present application, the Office Action of January 23, 2008, and the preparation of my concurrently filed Declaration Under 37 CFR §1.131, it became apparent that the facts and circumstances surrounding the development of this invention should be brought to the attention of the Examiner so that he or she may determine if they are material to this application under 37 CFR §1.56.

[0004] As part of a joint development program, TSMD and HP developed a sputter target and method of preparing same that could be used to form the heater layer in HP ink jet printer

heads. One of the requirements was that the targets had to have a density greater than 95% of the theoretical density and that the targets should be provided in a variety of target platform geometries. The density of powder consolidated targets is known to be related to particle performance. 100% density is ideal. HP manufactures thermal ink jet printer heads in many locations around the world, and each manufacturing location uses different sputtering tool sets requiring flexibility in target design and construction to match the various OEM platform designs.

[0005] During the project, several sintering aids were blended with tantalum silicon nitride powders followed by vacuum hot pressing (VHP) of the blends into shapes that could be machined in the final target shape. The challenge was to find sintering aids that would allow the blend to be pressure consolidated into a very dense mass without diminishing sputtering performance of the so formed sputter target.

[0006] Ultimately, we found that MgO and SiO_2 worked well as sintering aids and allowed us to achieve targets having densities of greater than 95% theoretical upon VHPing or HIPing of the powder blends.

[0007] The work conducted jointly by HP and TSMD was covered by a non-disclosure agreement. During the project, and more than one year prior to the priority date, a variety of candidate targets and target sizes were made by TSMD. These targets were shipped to HP and evaluated for sputtering performance and coating uniformity jointly by TSMD and HP. Several of these targets included either MgO or SiO_2 as sintering aids in blends containing W metal or Ta metal powders with Si_3N_4.

[0008] In order to help recover material costs, several of these targets were sold to HP during the project and these sales occurred more than one year prior to the priority date. Eventually, it was found that MgO worked best as a sintering aid, and a 12-inch diameter version of a W/Si_3N_4/MgO target was made by TSMD, sold and shipped to HP more than one year before the priority date. A drawing of this target is attached as Exhibit B (dates have been redacted) to my concurrently filed Declaration Under 37 CFR §1.131.

[0009] The target shown in Exhibit B was made with 60 atomic percent W, and 40 atomic percent silicon nitride (Si_3N_4) mixed with MgO in a ratio of 2 wt% MgO with respect to the Si_3N_4. The powders were blended in a V-cone blender and then screened through a minus 50 mesh screen. The screened powders were subjected to VHP under an inert Ar gas blanket with

temperatures in the press ramping up to 1640°C. The blend was pressure consolidated for about 120 minutes at a pressure of about 3950 lbs/in^2 (27.2 MPa). This target was tested, and the results were encouraging enough to further develop the process at HP. The goal of achieving 5600 micro-ohn-cm resistivity was achieved across production size wafers with uniformity better than 4%. Based on this success, other platform design targets were built on the Endura platform, initial test targets gave the desired resistivity but uniformity was not good; redeposition affected film properties, and target cracking was an issue. Several compositions, magnet pack geometries and edge profiles were attempted to develop a process that could yield better than 0.5% non-uniformity across 8" wafers consistently through target life.

[0010] As a result of this joint development and testing, HP issued its commercial specification to TSMD that established HP's requirements for 60/40 tungsten silicon nitride targets. This commercial specification was issued to TSMD prior to the priority due date but not before September 13, 2001. TSMD has sold targets to HP pursuant to this original specification and a few minor revisions to this original specification now for several years.

[0011] I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under §1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signature: _____ Date: June 23, 2008

David B. Smathers

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Sir/Madam:

Declaration Under 37 CFR §1.131

I, David B. Smathers, do declare and state as follows:

[0001] I received a Bachelor of Science Degree in Physics from Rhodes College, a Masters of Science Degree in Materials Science from the University of Wisconsin at Madison, and received my Doctor of Philosophy Degree in Materials Science from the University of Wisconsin, Madison.

[0002] I am presently the Director of Quality and Engineering at Tosoh SMD, Inc., one of the co-owners of the above patent application.

[0003] I am one of the named co-inventors of the above-identified patent application.

[0004] The inventors, including me, conceived and reduced to practice in the United States, the invention claimed in the above-identified patent application, prior to June 17, 2002.

[0005] Exhibit A attached is a copy of an invention disclosure that I executed along with one of the other co-inventors prior to June 17, 2002. This exhibit is evidence of both conception and actual reduction to practice of the claimed invention. Certain portions of this document have been redacted to remove non-relevant confidential subject matter and to conceal specific dates. This exhibit refers to a process for making sputtering targets wherein the claimed metal powder

and Si_3N_4 powder were blended with MgO or SiO sintering aids and that this blend was then pressure consolidated under heated conditions to form a blank of greater than 95% actual density.

[0006] One specific embodiment of this invention referred to on page 2 of the exhibit under portion "D" thereof refers to a tungsten, silicon nitride, magnesium oxide blend that was screened, vacuum hot pressed and ground into a sputter target blank. The blank was then solder bonded to a Cu/Cr backing plate using indium solder. A copy of the blueprint for this target is attached as Exhibit B with the date redacted. Accordingly, based on this information, the subject matter of the above identified application as claimed therein was conceived and reduced to practice prior to June 17, 2002.

[0007] I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under §1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signature: _____ Date: June 23, 2008

David B. Smathers

TOSOH SMD, INC.----------DISCLOSURE OF INVENTION

This is an important legal document. See opposite side for definitions of asterisked terms. The form should be carefully completed by the inventor(s) and forwarded in duplicate to the Patent Representatives

1. DESCRIPTIVE TITLE OF INVENTION

Process for Making Dense Mixed Metal-Si3N4 Targets

2. NAMES(S), TITLE(S) & HOME ADDRESS(ES) OF INVENTOR(S) include full middle name, COUNTRY of citizenship, and badge number.

David Bird Smathers, 3298 Kirkham Road, Columbus, OH 43123; U.S.A. Citizen; TSMD Badge 86459

Francis Samuel Valent, 6023 Epernay Way, Galloway, OH 43119; U.S.A. Citizen; TSMD Badge 86394

3. EMPLOYER: **Tosoh SMD, Inc. 3600 Gantz Road, Grove City, Ohio 43123 USA Phone 614-875-7912**

4. STAGE OF DEVELOPMENT	DATE (Month/Year)	LOCATION	IDENTIFY PERSONS OR RECORDS SUPPORTING FACTS IN 4.A-E
A. First disclosure to others		TSMD/HP	Proposal to Hewlett Packard under CDA
B. First sketch or drawing		TSMD/HP	Quotation
C. First written description		TSMD	Quotation/Order with Part Routing and B.O.M.
D. Completion of first model or device		TSMD /HP	Lot 9H0061-101 3" Sample
E. First actual reduction to practice		TSMD /HP	Lot 9H0101-101 RMX-12 Version

5. LIST PROJECT NUMBER AND OTHER PERTINENT NOTEBOOK ENTRIES, PHOTOGRAPHS, REPORTS, DRAWINGS:

NPD 780-1;804-1; 828-1; 871-1; 871-2; 871-4; 1042-1 All contain MgO

NPD 736-1; 737-1; 818-1; 858-1; 858-2 Contain no MgO or uses an Alternative (SiO)

Spreadsheet containing article attributes – Shared with HP and all versions are password protected.

Density Evaluation and Correction Document

Report on the evaluation of a used X-901 target to HP

HP Drafted a Specification in but it has never been issued and is currently being re-written by Garold Radke to cover current design.

TXRD Analysis of Targets for phase identification

6. IF THE INVENTION WAS DISCLOSED OUTSIDE OF TOSOH, identify the individuals, the companies or activities they represent, and the date of disclosure

Mike Regan, Hewlett Packard Corvallis, Advanced Research Lab, Lead Engineer

Jim Roberts, Hewlett Packard Corvallis, Advanced Research Lab, Procurement Specialist

Garold Radke, Hewlett Packard Corvallis, Advanced Research Lab, Lead Engineer

Bob Strain

Eldon Hilton

Judy Thompson

Marzio LeBan

7. LIST ANY KNOWN PUBLIC USE, PUBLICATION, OR ORAL PRESENTATION OF THE INVENTION, SALE OR OFFER FOR SALE

	No	Yes	Date	Persons, Companies, or Publications
A. Sold	X			Proprietary sale under CDA
B. Offered for sale as part of a product*	X			
C. Offered for sale in development program*		X		Several parts have been sold to HP to cover manufacturing expenses as HP works to determine composition and platform best suited to their process.
D. Described in a publication*	X			
E. Submitted to a publication*	X			
F. Placed in a public use*	X			
G. Used to make a product in public use	X			
H. Orally presented	X			

8. LIST DATES & DETAILS OF ACTIVITIES OF 7.A-H IF SCHEDULED IN THE FUTURE

9. RELATED GOVERNMENT CONTRACT(S) Did your job assignments involve work under a government contract related to the inventive subject matter at the time the invention was . . .

Conceived ? Yes____ NoX____ Contract Number_____

First successfully tested ? Yes____ No____ Contract Number_____

10. ATTACH A CONCISE TECHNICAL DESCRIPTION OF THE INVENTION. THE DESCRIPTION SHOULD INCLUDE:

A. General purpose of the invention
B. Prior art (previous) methods, materials, or devices performing function of the invention
C. Disadvantages of prior art
D. Identification of component parts, or steps, and explanation of mode of operation of invention
E. Alternate embodiments of the invention
F. Advantages of the invention over prior art
G. Features of the invention believed to be new
H. If a joint invention, the contribution of each inventor

The completed description should be signed by the inventor(s) and then read and signed by a technically competent witness, using the statement *DISCLOSED TO AND UNDERSTOOD BY ME THIS ___DAY___OF___19___." Drawings, sketches, photographs, reports, if available, may form a part of the disclosure, and reference thereto can be made to complete this description.

11. RECOMMENDED SECURITY CLASSIFICATION OF THE INVENTION

Unclassified Confidential Secret Other specify

12. SIGNATURE(S) OF INVENTOR(S) AND DATE

David B Smathers

Francis S. Valent

SIGNATURE(S) OF WITNESS(ES) AND DATE

J E Murphy

EXHIBIT

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A

Concise Technical Description of Invention

Descriptive Title: Process for Making Dense Mixed Metal-Si_3N_4 Targets

Inventor(s): David B. Smathers; Frank Valent

A. General Purpose of the Invention

As part of a joint development program with Hewlett Packard Ink Jet Business Unit Advanced Research Lab, TSMD developed metal/ceramic targets for the heater layer in ink jet printer heads. HP wanted mixtures of Ta-Al-O, Ta-Si-N or W-Si-N. The targets were required to be more than 95% dense and in a variety of target platform geometries.

The basic invention is a near full density Tungsten or Tantalum mixture with Silicon Nitride using the Vacuum Hot Press and a sintering aid. The choice for the sintering aid that works best is Magnesium Oxide between 0.05 to 4 weight percent with respect to the Silicon Nitride content.

B. Prior Art (previous) Methods, Materials, or Devices Performing Function on this Invention

The targets have been fabricated using VHP or HIP with low density results. Praxair MRC filed a patent on a HIP method using a pre-densification method. This did not work; the target was not dense and cracked during sputtering. According to Mark Gore, Unaxis also worked on this material using HIP without success.

C. Disadvantages of Prior Art

Without the sintering aid, the Silicon Nitride will not densify. The target material is not strong enough to support the bonding and sputtering operations.

At the temperatures required for densification of the ceramic, normal container materials can not be used. The blend can be compacted and covered with a glass prior to HIP. After HIP, the glass has to be machined off. The material efficiency is not as good as in the VHP since there is no external container to constrain the part.

D. Identification of Component Parts, or Steps, and Explanation of Mode of Operation of Invention

The target consists of a mixture of between 50 and 70 at% Tungsten and 50 to 30 at% Silicon Nitride. Magnesium Oxide is added to the Silicon Nitride at rate of 0.05 to 4 weight per cent with respect to the Silicon Nitride weight.

The Si_3N_4 is first mixed with the MgO. The mixture is –325 Mesh.

The Si_3N_4/MgO mixture is blended with the Tungsten powder. The Tungsten powder is –100 mesh but is made up of individual powder particles nominally 1 to 5 microns in size.

The mixture is screened through a –50 mesh screen multiple times (at least twice) to minimize the size of agglomerated Si3N4 to less than 300 microns in diameter. The MgO is hydroscopic and causes the mixture to absorb water and clump up.

The mixture is formed into a target blank using the Vacuum Hot Press according to recipe 16. The press operates at 800 torr/1640C during the peak of the cycle. The 800torr Argon backfill is required to keep the nitrogen from decomposing out of the Si_3N_4.

The target blank is ground to thickness and ground to diameter.

The target blank is solder bonded to a Cu1Cr backing plate using Indium solder.

E. Alternate Embodiments of the Invention

SiO may be used in large amounts to densify the target. More than 6 at% SiO is required to get the target density higher than 85%.

We could screen the powder under a protective atmosphere of nitrogen to limit the moisture pickup, use a variety of types of screening equipment designed to break up agglomerations such as a Sweeco vibrating head or use other powder blending techniques such as mechanical alloying to get better mixing of the different density components.

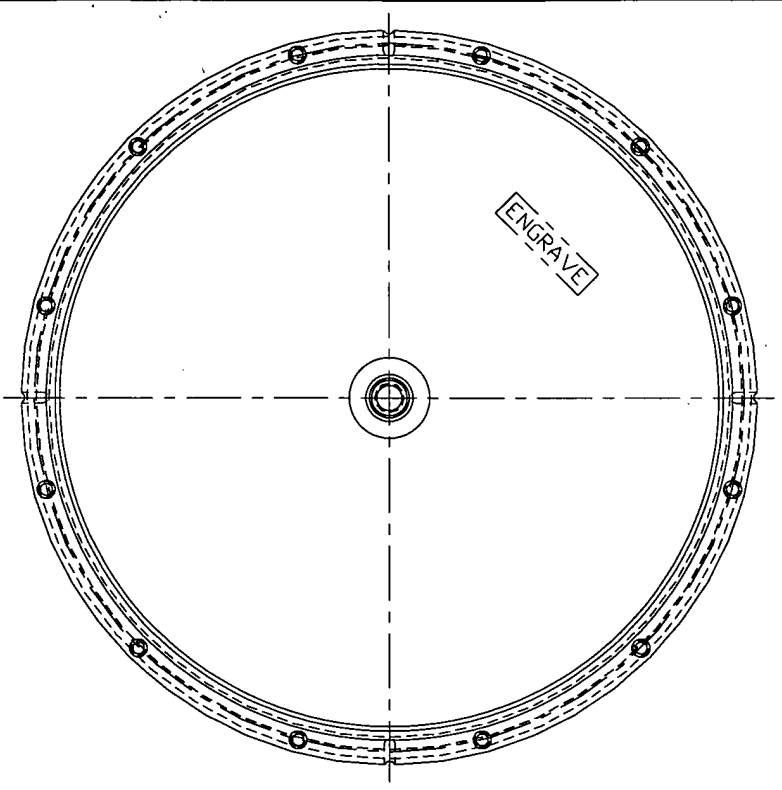
F. Advantages of the Invention Over the Prior Art

The MgO causes the Si_3N_4 to densify and the target stays intact during sputtering.
The VHP near net shape part improves material utilization.
The operation of the VHP at a slight over-pressure (800 torr) keeps the Nitrogen from escaping the mixture during the high temperature press cycle.

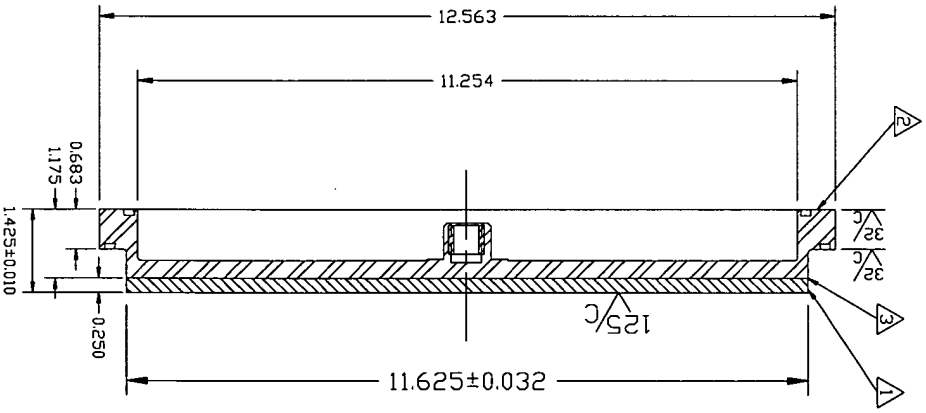
G. Features of the Invention Believed to be New

Inclusion of the MgO in the Si_3N_4/W mixture to form a dense sputtering target. The MgO does not harm the film in the application.
Screening of the mixture to control the Si_3N_4 agglomerates.
Operation of the metal mixture pressing under a protective atmosphere.

REV	DATE	DCN#



ITEM#	DESCRIPTION	QTY	PRINT#
1	TARGET	1	3110
2	B/P	1	3318
3	BOND MAT'L		



FOR H.P. ONLY

THIRD ANGLE PROJECTION

TOSOH SMD, INC.

UNLESS OTHERWISE SPECIFIED
DECIMALS .XX ± .01 .XXX ± .005
ANGULAR ± 1°
FRACTIONAL ± 1/64
DIMENSIONS ARE IN INCHES
DO NOT SCALE DRAWING
FINISH ✓

DRAWN KETTELL		DCN NO. R5051	TITLE BONDED ASSEMBLY
CHECK		DATE	B/A 12.563" ø X 1.175" B/P TO TGT
APPROVED		DATE	SIZE A / DWG NO 3262 / SHEET 1 OF 1
TSMD0217A.R1	SCALE NONE	REV. 0	

EXHIBIT
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